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X-Ray Photoelectron Spectroscopy Depth Profiling of As-Grown and Annealed Titanium Nitride Thin Films

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Abstract: Titanium nitride thin films were grown on Si(001) and fused silica substrates by radio frequency reactive magnetron sputtering. Post-growth annealing of the films was performed at different temperatures from 300 °C to 700 °C in nitrogen ambient. Films annealed at temperatures above 300 °C exhibit higher surface roughness, smaller grain size and better crystallinity compared to the as-grown film. Bandgap of the films decreased with the increase in the annealing temperature. Hall effect measurements revealed that all the films exhibit n-type conductivity and had high carrier concentration, which also increased slightly with the increase in the annealing temperature. A detailed depth profile study of the chemical composition of the film was performed by x-ray photoelectron spectroscopy confirming the formation of Ti-N bond and revealing the presence of chemisorbed oxygen in the films. Annealing in nitrogen ambient results in increased nitrogen vacancies and non-stoichiometric TiN films.

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1. Introduction

Titanium nitride (TiN) is a wide bandgap semiconductor with a wide range of interesting electrical and mechanical properties. Despite its wide bandgap, TiN has a high carrier concentration and hence TiN thin films can be used as a metal gate in microelectronic devices and can potentially be used as cathodes in electrochemical capacitors [1–4]. TiN is extremely hard-mechanical material and is often coated on drilling bits for its hardness and anticorrosive properties [5–7]. Moreover, TiN is not a toxic material and can be used in medical devices as well [8,9]. TiN exhibits both covalent and metallic bonds. Covalent bonds occur in the hybridized p and d orbitals, whereas metallic bonds occur in d orbitals. Due to the mixture of such bonding, TiN exhibits both metallic and semiconducting properties. For example, high electrical conductivity of TiN is due to the metallic bonding whereas hardness, high melting point and excellent chemical stability are due to its covalent bonding nature [10,11]. There are several reports on the growth of titanium nitride thin films by chemical vapor deposition (CVD) [12,13], pulsed laser deposition (PLD) [14–16], radio frequency (RF) and DC magnetron sputtering [17–21], molecular beam epitaxy (MBE) [22,23], ion beam assisted deposition [24] and atomic layer deposition [25]. TiN is reported to have n-type conductivity and a direct bandgap ranging from 2.7 eV to 4.06 eV. Bandgap variation in different reports is due to the difference in the growth conditions such as growth temperature, post growth treatment and N₂/Ar flux ratio [12,17,18,26].

Here, we report the influence of post-growth annealing temperature in nitrogen ambient on the structural, optical, electronic and chemical properties of titanium nitride thin films prepared by radio frequency (RF) magnetron sputtering. We report a detailed X-ray photoelectron spectroscopy (XPS) analysis and depth profiling of the as-grown and

annealed TiN thin films to understand the cause of variations in the reported bandgap values. Such a detailed depth profile study has been lacking in the reported work on TiN thin films.

2. Experimental Details

Titanium nitride thin films were prepared on fused silica and single crystal silicon (001) substrates simultaneously by RF magnetron sputtering (Oerlikon Univex 350, Leybold, Germany) of titanium target in the presence of flowing argon (Ar) and nitrogen (N₂) gases. Fused silica substrates were used for the optical transmittance measurements and the films grown on Si(001) were used for all the other characterization reported here.

Substrates were first chemically cleaned by sonicating them first in acetone and then in isopropanol before placing them in the sputtering chamber. The chamber was evacuated to an initial pressure of about $\sim 1.5 \times 10^{-5}$ torr by pumping for several hours. During the deposition, substrates were kept at room temperature and were continuously rotated at six revolutions per minute for uniform thin film growth. Argon (99.999% pure) and N₂ (99.99% pure) were used as sputtering gas and reactive gas respectively. Flow rate of Ar and N₂ during the growth were fixed at 60 and 10 standard cubic centimeters per minute (sccm), respectively. Titanium (99.99% pure) target was sputtered by setting the RF power to 100 Watt. During the growth, chamber pressure was maintained at 5.4×10^{-3} torr and the deposition time was about one hour. After the growth, films were taken out of the chamber and placed in a furnace for annealing in the presence of nitrogen ambient at a N₂ flow rate of 100 sccm. One film was not annealed and the other three films were annealed at a temperature of 300, 500, and 700 °C respectively. During the annealing, temperature was ramped at a rate of 5 °C/min and after reaching the desired temperature, samples were kept at that temperature for three hours and then the furnace heater was turned off. The samples were kept inside the furnace under nitrogen ambient until the samples reached room temperature.

Surface morphology of the films was studied by atomic force microscopy (AFM) using non-contact mode or tapping mode (Veeco Innova diSPM by Bruker, Billerica, MA, USA). AFM images were processed by applying three-point leveling to remove the unevenness in the appearance of the raw images that are due to small tilt in the substrate. Laplacian algorithm was used to mark the grains and the grain size was estimated by selecting the appropriate threshold that would result in a maximum number of grains in the grain statistics. Average threshold value for our samples was around 50% [27,28]. Crystal structure of the films was studied using x-ray diffraction (Shimadzu XRD-6000 diffractometer, Kyoto, Japan equipped with Cu-K_α radiations of wavelength 1.548 Å). Normal incidence transmittance spectra of the samples were acquired in the range of 200 to 2000 nm by a UV-Visible Jasco V-570 spectrophotometer (Easton, MD 21601, USA). Hall effect measurements of the films were carried out using the four-probe Van der Pauw method [29]. Hall measurements were performed at room temperature using the ECOPIA HMS3000 system (Gyeonggi-do, Korea). Electrical contacts to the films were made using silver paint. Chemical composition of the films was determined by X-ray Photoelectron Spectroscopy (XPS), using a Thermo Fisher ESCALAB 250Xi spectrometer (Waltham, MA, USA) equipped with Al-K_α source and the chamber pressure was about 4×10^{-10} Torr. Depth profiling was performed by etching the surface of the films by bombarding them with argon ions of energy 3 KeV for 30 s. After each etching cycle, high-resolution XPS spectra for titanium (Ti2p), nitrogen (N1s) and oxygen (O1s) were acquired. Etching was performed until the film–substrate interface was reached.

3. Results and Discussions

Shown in Figure 1 are the XRD θ -2 θ scans of the as-grown and the annealed samples. The XRD scan of S1 (as-grown) contains Si(001) peak along with TiN(220) and TiN(200) peaks. Highest intensity XRD peak of the film is of TiN(220), indicating the preferred growth direction for TiN film is along (220). XRD scan also contains a small peak of

TiO₂(118) indicating the presence of oxygen in the film. Oxygen could be present in the chamber during the growth or it was chemisorbed on the surface when samples were exposed to air after the growth. It is quite unlikely for oxygen to be present during the growth because the chamber was evacuated for several hours prior to the growth to a pressure of $\sim 1.5 \times 10^{-5}$ torr. Moreover, highly pure argon and nitrogen gasses were used to ensure the high purity of the films. So most likely, oxygen was chemisorbed after the growth when the samples were exposed to air.

Figure 1. XRD scans of S1 (as-grown), S2 (annealed at 300 °C), S3 (annealed at 500 °C) and S4 (annealed at 700 °C) TiN thin films.

XRD scans of the annealed samples (S2, S3 and S4) contain TiN (111) and TiN (222) peaks along with TiN (200) and TiN (220) with preferred orientation along TiN(220). There is also a noticeable increase in the number of TiO₂ phases. XRD spectra reveal that the crystal structure of all TiN thin films is face centered cubic (FCC) [18]. The lattice constants of TiN films were calculated using Bragg's equation:

$$n\lambda = 2d \sin\theta \quad (1)$$

where $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$.

The lattice constants were found to be 4.18, 4.16, 4.16 and 4.17 Å for S1, S2, S3 and S4, respectively, indicating a little effect of annealing on the lattice constant of the films. These values are considerably close to the reported values of TiN lattice constant of 4.20 and 4.22 Å [30].

Full width at half maximum (FWHM) for TiN(200) peak decreases with the increase in the annealing temperature. It was found to be 0.50, 0.23, 0.22 and 0.21 degrees for S1, S2, S3

and S4, respectively. A decrease in the FWHM of TiN(200) peak due to post growth annealing is an indication of increased crystallinity of the film along (200) direction. However, there was no significant change in the FWHM of TiN(222) and TiN(220) XRD peaks.

Surface morphology of the films was studied using atomic force microscopy. Two- and three-dimensional $5 \times 5 \mu\text{m}^2$ AFM images of as-grown and annealed films on Si (001) substrate are shown in Figure 2a–h. Root mean square (RMS) roughness and the average grain size of the films as calculated from these images are given in Table 1. Surface morphology of the as-grown titanium nitride thin film is mostly smooth two-dimensional with few bright protrusions on the surface, which appear as column like structures in the 3D image. For sample S2, these protrusions increase in number, width and height relative to their adjacent surroundings ranging between 8 and 13 nm in height. These protrusions could be due to elemental titanium agglomerating on the surface. For sample S3 that was annealed at 500 °C, the number of protrusions is reduced but the surface roughness has increased more than 60%. Surface morphology of the sample annealed at 700 °C is quite different compared to the other samples annealed at lower temperature. The whole surface consists column-like features, an indication that the sample becomes more vertically oriented. Annealing at high temperature transforms the surface from a 2D to 3D columnar surface.

Figure 2. Atomic force microscopy (AFM) images of TiN thin films: (a,b) S1, as-grown, (c,d) S2, annealed at 300 °C, (e,f) S3, annealed at 500 °C, (g,h) S4, annealed at 700 °C.

Table 1. Root mean square (RMS) surface roughness, average grain size as measured by AFM images, optical, and electrical properties of TiN films.

Sample	Annealing (°C)	RMS Surface Roughness (nm)	Average Grain Size (nm)	Band Gap (eV)	Carrier Concentration (cm ⁻³)	Resistivity (Ω.cm)
S1	As-grown	0.505	11.20	3.67	9×10^{18}	3.0×10^{-4}
S2	300	0.506	11.22	3.56	7×10^{18}	9.0×10^{-4}
S3	500	0.821	9.245	3.53	1×10^{19}	20×10^{-4}
S4	700	1.648	9.418	3.52	7×10^{19}	2.0×10^{-4}

UV-Visible transmittance spectra were acquired for the as-grown and the annealed TiN films grown on the fused silica substrates. The optical bandgap (E_g) of the films was determined using the following equation: $(\alpha_c E)^z = \beta_c(E - E_g)$, where β_c is a constant, E is the photon energy, and z is power factor of value 2 for the direct bandgap material and $1/2$ for indirect bandgap. Figure 3 is a plot of $(\alpha E)^2$ as a function of photon energy (Tauc plot) of as-grown and annealed TiN films. The extrapolation of the linear portion of the curves to the horizontal axis provides the bandgap values of the films, which are listed in Table 1. Bandgap of the as-grown TiN film is 3.67 eV, which is close to the reported values [17,31]. The bandgap of the annealed films decreases with the increase in the annealing temperature. Bandgap of the annealed films becomes closer to the TiO₂ values because at high annealing temperature the Ti-N bond is broken and nitrogen is replaced by oxygen, forming TiO₂, which was also observed in the XRD.

Figure 3. Tauc plots of the as-grown and the annealed TiN thin films.

Hall effect measurements revealed that all the films have n-type conductivity with high carrier concentration that increases slightly with the increase in the annealing temperature. The carrier concentration and resistivity values obtained are summarized in Table 1. High carrier concentration in titanium nitride has been attributed to the shallow donor level of the fourth valence electron of titanium not participating in the covalent bonding with nitrogen [17].

Films annealed at 300 and 500 °C have slightly higher resistivity compared to the as-grown film and the film annealed at 700 °C. An increase in the resistivity can be attributed to the presence of TiN(111) lattice plane. This plane exhibits a rougher surface which increases charge scattering, resulting in increased resistivity [14]. This plane was found in

the XRD patterns of the samples annealed at 300 and 500 °C but was absent in the XRD of at 700 °C.

X-ray photoelectron spectroscopy (XPS) was performed to determine the chemical composition of the films and the oxidation states of different elements in the films. To study the presence of different elements throughout the thickness of the films, depth profiling was performed by etching the film's surface by low energy Ar ions for 30 s repeatedly and high-resolution spectra of Ti2p, O1s and N1s were obtained after each etching cycle.

Shown in Figure 4 is a wide-scan XPS spectrum of the as-grown TiN film. The spectrum contains Ti2p, N1s, C1s, O2p and Ar2p peaks. Presence of Ar2p peak in the spectrum is due to the use of Ar ions for etching the film during XPS acquisition. The presence of C1s peak is due to organic contamination of the sample when exposed to air after the growth. C1s binding energy of 284.8 eV is used as a reference to correct the XPS spectra due to any charging effect.

Figure 4. A wide-scan XPS spectrum of as-grown TiN film.

Shown in Figure 5a is N1s spectrum of as-grown TiN film. Peak fitting of the N1s spectrum reveals that the spectrum can be deconvoluted into two peaks, one is due to Ti-N bond and the other relatively small peak can be attributed to titanium oxynitride Ti-O-N. High-resolution XPS spectra of N1s of all the samples are shown in Figure 5b. N1s peaks corresponding to Ti-N for as-grown and samples annealed at 300 and 500 °C are centered at 396.8 eV, 396.6 eV, and 397.4 eV, respectively [20,30,32]. The signal of N1s in the XPS spectrum of the sample annealed at 700 °C is too weak to determine the peak position indicating there is relatively less nitrogen in the sample. This could be due to breaking of Ti-N bond at high annealing temperature and exodus of nitrogen from the film. This is consistent with the XRD data where the intensity of TiN (200) peak is much smaller compared to the TiN(200) peak intensity in the other samples. The second peak of nitrogen in the N1s spectra for the as-grown and for the samples annealed at 300 °C, is centered on 398.5 and 398.6 eV, which correspond to Ti-O-N formation [30,32]. Shown in Figure 5c is N1s spectra taken at different depths in the film by Ar ion etching. N1s spectra at different depths show an increase in the intensity of the peak after each etching cycle indicating more nitrogen is present in the bulk compared to the surface layers of the film. This could be due to chemisorption of oxygen from the environment resulting in oxygen occupying nitrogen position in the surface layers.

Figure 5. (a) High resolution XPS spectrum of N1s of as-grown TiN film; by peak fitting the spectrum is deconvoluted in TiN and TiN_xO_y peaks. (b) High resolution XPS spectra of N1s of as-grown and annealed TiN films, taken after 30 s etching. (c) High resolution XPS spectra of N1s of as-grown TiN film, taken at different etching levels.

Due to spin-orbit coupling, Ti2p consists of two peaks in the XPS spectra, Ti2p_{3/2} and Ti2p_{1/2}. Shown in Figure 6a is only the Ti2p_{3/2} peak for all the samples. Ti2p_{3/2} peaks of all the films can be deconvoluted into three different peaks, as shown in Figure 6b; the peak positions of the deconvoluted peaks are given in Table 2. The peak positions correspond to the binding energy of Ti-O₂, Ti-O-N and Ti-N [19,30,32,33]. Shown in Figure 6c is the Ti2p_{3/2} spectra at different depth levels in the as-grown film. In the first few surface layers, the Ti2p_{3/2} peak consists of Ti-O₂, Ti-O-N and Ti-N peaks, but in the bulk, the Ti-O₂ peak disappears and instead the elemental Ti peak emerges, as shown in Figure 7. This also confirms that oxygen was chemisorbed in the film from the atmosphere after the growth. Annealing the sample at high temperature results in breaking of the Ti-N bond and formation of the Ti-O₂ bond because bond formation energy of Ti-O₂ is less than Ti-N bond formation. Enthalpy of TiN is −265.8 KJ/mol, whereas for TiO₂ it is −944.0 KJ/mol [34]. Therefore, near the surface where oxygen is available, the Ti-O₂ bond is formed and deeper in the film where oxygen is not available after breaking of Ti-N bond, nitrogen may form N₂, leaving behind elemental Ti.

Figure 6. (a–c): (a) High resolution XPS spectra of Ti2p_{3/2} of as-grown and annealed TiN films, taken after 30 s etching. (b) Peak fitting of high resolution XPS spectrum of Ti2p_{3/2} of as-grown TiN film. (c) High resolution XPS spectra of Ti2p_{3/2} of as-grown TiN film, taken at different etching level.

A plot of N1s/Ti2p_{3/2} peak atomic ratio as a function of etching time is shown in Figure 8. N1s/Ti2p_{3/2} peak intensity ratio increases deeper in the film for as-grown TiN film. In the case of annealed films, however, this ratio either decreases slightly or stays constant. This also confirms the fact that post-growth annealing results in breaking of the Ti-N bond, resulting in nitrogen exiting the film and leaving behind elemental titanium, which increases the chances of the film being oxidized by atmospheric oxygen. This is consistent with the XRD results where Ti-O₂ phases were found in the annealed samples but not in the as-grown samples.

Table 2. Peak positions of deconvoluted $Ti2p_{3/2}$.

Sample	Etching Time (s)	Ti-O ₂ (eV)	Ti-O-N (eV)	Ti-N (eV)	Ti (eV)
S1	30	459.0	457.6	456.5	
S2		459.0	458.2	456.8	
S3		458.6	457.5	456.3	
S4		459.2	458.5	457.0	
S1	90	458.6	457.0	455.6	
S2		458.5	456.8	455.3	
S3		458.0	456.5	455.2	
S4		458.3	456.6	455.1	
S1	150	458.3	456.6	455.2	
S2			457.6	456.0	454.8
S3			457.3	455.9	454.6
S4			457.9	456.1	454.7
S1	210	458.1	456.3	454.5	
S2			457.6	455.9	454.7
S3			457.3	455.9	454.5
S4			457.8	456.0	454.7

Figure 7. (a–d): Peak fitting of high resolution XPS spectrum of $Ti2p_{3/2}$ of S2 (annealed at 300 °C) TiN film: (a) taken after 30 s etching; (b) taken after 90 s etching; (c) taken after 150 s etching; (d) taken after 210 s etching.

Figure 8. N1s/Ti2p_{3/2} atomic ratio as a function of etching time of as-grown and annealed TiN films.

4. Conclusions

Titanium nitride thin films were prepared by RF magnetron sputtering of Ti target in N₂ and Ar mixture of gases at room temperature followed by the post-growth annealing at different temperatures in nitrogen ambient. Structural and electrical properties were extremely dependent on the post growth annealing treatment. Annealing seemed to enhance the crystallinity of the films. Surface roughness increased, and the average grain size decreased with the increase in the annealing temperatures. Optical bandgap of the as-grown TiN thin film was 3.67 eV and it decrease consistently with the increase in the post growth annealing temperature. We found that post-growth annealing in nitrogen ambient, although enhancing the crystallinity of the TiN films, also results in an increase of TiO₂ phases. All of the films exhibited n-type conductivity and the carrier concentration increased with the increase in the annealing temperature. XPS study of the films confirms the formation of Ti-N bonds along with TiO₂ formation due to chemisorbed oxygen in the surface layers. Depth profiling of the film revealed that intensity of N1s peak increased whereas O1s peak decreased with each etching level. As-grown film has stoichiometric TiN, whereas annealed films had less than stoichiometric nitrogen in the film, indicating breaking of Ti-N bond at high annealing temperatures.

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